

PATENT SPECIFICATION

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NO DRAWINGS

(21) Application No. 54110/69 (22) Filed 5 Nov. 1969

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C1M 11B1 11C1 11C10 11C11 11C3 11C4 11C5 11C6
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(54) PROCESS FOR TREATING GLASS

(71) I, ARTHUR TERENCE RAN-
SON, a British Subject, of 12 Church Street,
Liverpool, 1, Lancashire, do hereby declare
the invention, which was communicated from
5 Owens-Illinois, Inc., a corporation organised
and existing under the laws of the State of
Ohio, United States of America, of Toledo,
State of Ohio, United States of America, for
which I pray that a patent may be granted to
10 me, and the method by which it is to be
performed, to be particularly described in and
by the following statement:—

article. Lithium ions in a glass have been
exchanged alternatively with sodium and potas- 50
sium ions in molten inorganic salt baths.
Sodium ions in glass have been exchanged with
lithium and potassium ions of molten salt
baths containing lithium and potassium in-
organic salts. 55

Alkali metal ions have different ionic dia-
meters as can be seen on page 900 of the 3rd.
edition of Van Nostrand's Scientific Encyclo-
pedia, published in 1958 by D. Van Nostrand
Co. Inc., Princeton, N.J. The lithium ion has 60
the smallest ionic diameter. The ionic dia-

SPECIFICATION NO 1294337

1 By a direction given under Section 17 (1) of the Patents Act 1949 this application
proceeded in the name of OWENS-ILLINOIS, INC., a Corporation organised and existing
under the laws of the State of Ohio, United States of America, of Toledo, State of
2 Ohio, United States of America.

THE PATENT OFFICE

R 14339 /7

25 coloring oxides such as oxides of iron, cobalt,
nickel, manganese, chromium and vanadium,
and fining agents, and also especially relates
to the silicate glass article resulting from the
treatment by the present process.

30 As used herein, the term "glass" is in-
tended to include glass that is controllably
crystallizable, commonly referred to as a
thermally crystallizable glass composition, and
crystallized glass, commonly referred to as
35 a glass-ceramic, as well as conventional glasses
which are essentially entirely vitreous in nature.

40 As described later in detail many types of
silicate glasses, including glass-ceramics, that
contain alkali metal ions have been treated at
an elevated temperature by contact with an
alkali metal inorganic salt for exchange of
45 alkali metal ions in a surface portion of the
glass with alkali metal ions of the inorganic
salt. The usual process is an immersion of
the glass in a molten bath of alkali metal in-
organic salt or of a mixture of the alkali metal
inorganic salt with other inorganic salts. The
time of immersion is sufficient to cause this
exchange only in a surface layer of the glass

spaces previously occupied by the smaller
alkali metal ions, thereby creating the com-
pressional stress in the surface layer. Because
the temperature of the glass is below the
strain point, the glass structure cannot readjust
itself to relieve the stress. 75

When a smaller alkali metal ion replaces a
larger alkali metal ion in the surface layer of
the glass the expansion coefficient of the sur-
face layer will be changed to a lower value
than that of the interior part of the glass
article, with the result that the surface layer
has a compressional stress. This ion exchange
can be carried out at a temperature either 80
below the strain point or at a temperature
above the strain point but below the softening
point of the glass. When the process of ion
exchange is carried out below the strain point
to replace a larger alkali metal ion in the glass 85
with a smaller alkali metal ion, then the
article after the exchange is then heated to a
temperature sufficiently above the strain point
to heal strength-reducing minute cracks occur-
ring during the ion exchange treatment, due 90
to the difference in the expansion coefficients 95

[Price 25p]

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which I pray that a patent may be granted to
10 me, and the method by which it is to be
performed, to be particularly described in and
by the following statement:—

This invention relates to a process for treat-
ing articles of glass, including glass components
15 of articles, to improve the strength of the
glass articles and also relates to the articles
resulting from the treatment by the process.
The present invention especially relates to a
process for treating silicate glass composed of
20 silica and an alkali metal oxide or oxides,
with or without one or more other compatible
constituents such as alkaline earth metal oxides,
alumina, zirconia, titania, boron oxide, glass
coloring oxides such as oxides of iron, cobalt,
25 nickel, manganese, chromium and vanadium,
and fining agents, and also especially relates
to the silicate glass article resulting from the
treatment by the present process.

As used herein, the term "glass" is in-
tended to include glass that is controllably
30 crystallizable, commonly referred to as a
thermally crystallizable glass composition, and
crystallized glass, commonly referred to as
a glass-ceramic, as well as conventional glasses
35 which are essentially entirely vitreous in nature.

As described later in detail many types of
silicate glasses, including glass-ceramics, that
contain alkali metal ions have been treated at
an elevated temperature by contact with an
40 alkali metal inorganic salt for exchange of
alkali metal ions in a surface portion of the
glass with alkali metal ions of the inorganic
salt. The usual process is an immersion of
the glass in a molten bath of alkali metal in-
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article. Lithium ions in a glass have been
exchanged alternatively with sodium and potas-
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Sodium ions in glass have been exchanged with
lithium and potassium ions of molten salt
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Alkali metal ions have different ionic di-
ameters as can be seen on page 900 of the 3rd.
edition of Van Nostrand's Scientific Encyclo-
pedia, published in 1958 by D. Van Nostrand
Co. Inc., Princeton, N.J. The lithium ion has
the smallest ionic diameter. The ionic di-
ameters of the other alkali metal ions are in the
order: sodium, potassium, rubidium and
cesium, with cesium having the largest ionic
diameter.

When a larger alkali metal ion replaces a
smaller alkali metal ion in the surface layer of
glass at a temperature that is below the strain
point of the glass, the surface layer then has a
compressional or compressive stress.
Apparently the larger ions occupy the smaller
spaces previously occupied by the smaller
alkali metal ions, thereby creating the com-
pressional stress in the surface layer. Because
the temperature of the glass is below the
strain point, the glass structure cannot readjust
itself to relieve the stress.

When a smaller alkali metal ion replaces a
larger alkali metal ion in the surface layer of
the glass the expansion coefficient of the sur-
face layer will be changed to a lower value
than that of the interior part of the glass
article, with the result that the surface layer
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to replace a larger alkali metal ion in the glass
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article after the exchange is then heated to a
temperature sufficiently above the strain point
to heal strength-reducing minute cracks occur-
ring during the ion exchange treatment, due
to the difference in the expansion coefficients

[Price 25p]

of the interior and the surface layer. Then the stress and the resultant improved strength in the final product will be due to the compositional difference. When there is obtained by the ion exchange a surface layer that has a substantially lower co-efficient of expansion that that of the interior glass, the ion exchange is performed as near to, but still below, the strain point as feasible, to avoid the creation of substantial cracks that would not be healed by the latter heating to a temperature above the strain point.

S. S. Kistler in a paper in the Journal of the American Ceramic Society, 45, No. 2, at pages 59—68, and Research Corp. in British Patent No. 917,388 describe an ion exchange process. The British Patent mentions the following specific alkali metal inorganic salts that are suitable: NaNO_3 ; KSCN ; KNO_3 ; $\text{K}_2\text{S}_2\text{O}_7$; RbNO_3 . These are used in a molten form or as a solution in an organic, non-aqueous ionizing solvent, e.g. acetamide.

U.S. Patent No. 2,779,136 lists various alkali metal salts for use in molten form to ion exchange with alkali metal ions of a glass. Only two of these are the salts of an inorganic acid and lithium used alone, i.e., without admixture with other alkali metal salts. These two salts require the use of substantially high temperatures because of their high melting points. The melting points are reduced by mixing such salts with other alkali metal salts or alkaline earth metal salts. Even in such cases, the temperatures that have been used for the ion exchange are still high, presumably due to the high melting points of such mixtures.

These alkali metal salts of inorganic acids can be corrosive at the ion exchange temperature. Furthermore, the melting point can change with a substantial change in the alkali metal composition of the bath due to the ion exchange. In the latter case, when a larger alkali metal ion in the bath is replacing a smaller alkali metal ion in the glass, the melting point of the bath can increase substantially, so that the bath can be used at a temperature just above the melting point of the initial bath composition for only a limited period of time. It is desirable that the ion exchange be carried out with the bath until the alkali metal ion from the glass is no greater than 5% of the alkali metal content on a mole basis; otherwise, the salt bath will become unsuitable for further ion exchange. In view of the high temperatures required to melt some alkali metal inorganic salts they are not suitable for use alone at temperatures below the strain point of many glasses.

According to the present invention there is provided a process for treating an article composed of an inorganic glass (as hereinbefore defined) containing an alkali metal oxide, which process comprises contacting a surface of said glass with a non-polar, non-ionic liquid

medium containing a different alkali metal as a salt of an organic acid at an elevated temperature and for a period of time sufficient for some of said alkali metal in the surface layer only to exchange with some of said different alkali metal in said salt, removing the salt, and cooling the glass article.

Preferably, the glass is a silicate glass and the alkali metal oxide in the glass constitutes at least 1% by weight of the glass at least in the surface layer.

The liquid medium preferably comprises at least one non-polar, non-ionic organic compound as a major constituent and the salt as a minor constituent.

In one preferred embodiment, the salt is sodium acetate, the alkali metal in the glass is lithium and the elevated temperature is below the strain point of the glass, e.g. between 200°C and 550°C or, preferably, between 300°C and 430° . The time of treatment is advantageously at least three hours.

In another preferred embodiment the salt is potassium acetate, the glass is a soda-alumina-silica glass containing titania and the elevated temperature is below the strain point of the glass, e.g. between 371°C (700°F) and 400°C (750°F), advantageously for at least three hours.

The invention also provides a process for treating an article composed of a glass containing as its ingredients the following in weight percent ranges:—

SiO_2	35—88	
M_2O	1—48	100
Al_2O_3	0—40	
CaO	0—15	
MgO	0—28	
BaO	0—15	
SrO	0—15	105
B_2O_3	0—15	
ZrO_2	0—25	
TiO_2	0—12	
SnO_2	0—2	
P_2O_5	0—10	110
As_2O_3	0—3	
Sb_2O_3	0—3	the balance, if any

being other compatible ingredients and wherein M_2O refers to the total of alkali metal oxide, which comprises immersing for a period of time the glass article in a liquid body of a non-polar, non-ionizing organic vehicle containing as a minor percentage an alkali metal salt of an organic acid while maintaining said body at an elevated temperature, said alkali metal of said salt being a different chemical element than an alkali metal present in said glass in an amount of at least 1% by weight expressed as oxide, and said temperature and time being sufficient for ion-exchange by said different chemical elements to occur between a surface layer only of said glass and said salt in said liquid body of an organic vehicle,

removing the glass article, and removing any adhering organic vehicle and salt. Preferably the organic vehicle is a hydrocarbon material e.g. paraffin wax, the organic acid of the salt is a carboxylic acid, the temperature is between 300°C and 430°C and the period of time of immersion is at least three hours. The minor percentage may be less than 1% by weight, the alkali metal in the glass may be lithium and the salt may be sodium acetate. The glass used in this process may be a thermally crystallizable glass or an opaque glass ceramic containing a multiplicity of crystals each being less than 30 microns across its largest dimension, and having an average lineal coefficient of thermal expansion that is less than 20×10^{-7} per °C (between 25°C and 300°C). In another form of this process the salt may be potassium acetate and the glass may be a soda-silica composition containing titania. The process of the invention may be carried out at a relatively low temperature and the ion exchange medium may be in diluted form in which the diluent is liquid at the low temperature without introducing other metal ions.

Whilst not wishing to be bound by any theory, the applicants believe that the article comes into contact with a separate liquid body of said alkali metal salt of an organic acid even though this body is intermingled with the carrier vehicle.

The process may utilise a material for ion exchange with glass in which the alkali metal ion content of the material contacting the glass can be quite low so that the cost of material is less than with materials heretofore used.

The ion exchange medium used may be less corrosive than materials heretofore used.

An advantage of the process of the invention is that ions displaced from the glass may be easily separated from the medium contacting the glass for reuse of the contacting medium.

The alkali metal salts are salts of organic acids, for example, carboxylic acids and sulfonic acids. The carboxylic acids, can be, e.g. aliphatic acids having 1 to 22 carbon atoms, e.g. formic acid, acetic acid, propionic acid, caproic acid, neodecanoic acid and stearic acid, aromatic carboxylic acids, e.g. benzoic acid and toluic acid, and naphthenic acids. Examples of sulfonic acids are ethane sulfonic acid, benzene sulfonic acid, toluene sulfonic acid and those two classes of sulfonic acids obtained by sulfuric acid treatment of hydrocarbon oils, e.g., in the manufacture of water-white mineral oil. The two classes are in their sodium salt form known as water-soluble sulfonate soap and oil-soluble-sulfenate soap. When the organic acid has a relatively large number of carbon atoms the thermal stability is less than that of the organic acids having a small number of carbon atoms so that the use of the higher molecular weight acids is limited to lower temperatures or for a decreased period of time.

It is preferred that the alkali metal salt be one of acetic acid.

It is further preferred that the salt be used with an organic vehicle. The organic vehicle is a non-polar, non-ionic compound or mixture of such compounds. The organic vehicle is used with the alkali metal salt of the organic acid dispersed in it or dissolved in it, depending upon the organic compound and salt that are chosen. The organic vehicle should preferably be liquid at a temperature substantially below 200°C. and should be liquid at the ion exchange process temperature at least under superatmospheric pressure, preferably provided by nitrogen or other inert gas. Suitable vehicles should be at most only partially decomposed during the ion exchange treatment. Non-polar organic compounds are preferred. Examples of suitable vehicles are paraffinic hydrocarbon oils, paraffin wax or wax fractions having relatively high melting points, i.e., above 150° F., aromatic polynuclear hydrocarbons including diphenyl, and aromatic ethers such as diphenyl oxide and, of course, compatible mixtures thereof such as the eutectic mixture of diphenyl and diphenyl oxide.

The alkali metal salt of an organic acid alone or in the organic vehicle is used at an elevated temperature, between 200 and 550°C. (between 380 and 1000°F), preferably between 300 and 430°C. (between 570 and 800°F). Using sodium acetate or potassium acetate with the organic vehicle at 371° to 400°C (700 to 750°F.), 3 to 5 hours contact will give a layer not substantially affected by the abrasion test. The length of time in which there is contact with a glass surface for ion exchange is dependent upon: (1) the temperature; (2) the type of ion exchange, that is, whether a smaller or larger alkali metal ion is being displaced from the glass surface portion; (3) the composition of the glass; (4) whether it is a glass-ceramic; and (5) the depth of the surface layer in which the ion exchange is to be accomplished. Accordingly, the time can be as short as a few minutes or it can be carried out for a substantial number of hours, e.g. 10 hours. Also the time is determined to some extent by the degree of dilution, if any, of the alkali metal salt of the organic acid afforded by the organic vehicle. Surprisingly, in the case where the alkali metal salt of the organic acid is not very soluble or dispersable in the organic vehicle at the temperatures used for ion exchange good ion exchange can be obtained by contacting the organic vehicle containing this small amount of salt therein with the glass at the ion exchange temperature. For example, sodium and potassium acetates are almost insoluble or nondispersable in paraffinic hydrocarbon oil and paraffin wax. At 380°C. each of these acetates in a vessel with the oil or wax will be present as a slower separate heavier liquid phase. The alkali

metal acetate content in the oil or molten wax will be below 0.1% by weight when 10 parts of the acetate is at 380°C. in a vessel also containing 90 parts of either organic vehicle. It is preferred that the overall content in the treating vessel comprise at least 1% by weight of alkali metal acetate and the balance being essentially the organic vehicle.

There is a distinct advantage in the use of the combination of the organic vehicle and the alkali metal salt of an organic acid that is only very slightly soluble or dispersible in the organic vehicle at the elevated temperature used for ion exchange. After the exchange, the organic vehicle now contains organic acids as salts of two alkali metal ions, the new ion being that displaced from the glass and replacing that part of the initial alkali metal ion now in the glass apparently on an equimolar basis. The vehicle is now contaminated or poisoned with the new ion insofar as further use is concerned. However, the vehicle, after separation from liquid alkali metal salt, if present as another lower liquid phase, is cooled to a temperature (which may be below 100°C.) at which the mixture of alkali metal salts will crystallize out of the vehicle. After filtration, the filtrate, i.e., organic vehicle can be reused.

The following examples illustrate the preferred embodiment of the present invention using three types of glass. Gobs of glass, obtained from a furnace melt, were remelted in a platinum pot. Glass cane was pulled from this molten glass and 5-inch long sample rods were made from the cane by cutting. The sample rods had a diameter of about 3/16 inch. Some of the sample rods were tested for flexural strength, with or without an abrasion. Other sample rods were ion exchanged by the process of the present invention, followed by gradual cooling to avoid the creation of thermal stress, which itself increases glass strength, and then followed by non-abrasive removal of all coating, i.e. oil and salt, on the glass of the treating medium. In example I, owing to the glass being of the type that is controllably crystallized by a heat treatment, some of the sample rods were converted to glass-ceramics prior to the ion exchange treatment.

The abrasion of rods comprised tumbling them for 15 minutes in a ball mill containing No. 30 silicon carbide grit.

The flexural strengths or modulus of rupture were determined using a Tinius-Olsen Testing Machine. This machine applies a measured load through a single knife edge to the center of a sample rod supported on two knife edges which are four inches apart (3-point loading). The load is applied at a constant rate of 24 lbs. per min. until failure occurs with a marker indicating the highest load applied to the point of failure. A dial micrometer calibrated in inches and equipped with a bore contact instead of a point

contact is used to measure the maximum and minimum diameters at the center of the sample to an accuracy of 0.0005 inches. Since few sample rods are perfectly round, the load is applied normal to the maximum diameter and the standard formula for an elliptical cross-section is used in calculating the modulus of rupture as follows:

$$MR = \frac{(10.185) \times \text{Load}}{D_1^2 \times D_2}$$

The modulus of rupture in this formula gives the flexural strength in pounds per square inch of cross-sectional area at failure.

Example 1

A glass of the following analyzed composition in percent by weight was obtained by melting batch materials in a large continuous furnace:

SiO ₂	71.3	
Al ₂ O ₃	17	
TiO ₂	1.8	85
MgO	4	
Li ₂ O	3.5	
ZrO ₂	1.3	
P ₂ O ₅	1.5	
F ₂	0.1	90
As ₂ O ₃	0.2	
Fe ₂ O ₃	0.03	

This glass is similar in composition to a glass disclosed in U.S. Patent No. 3,380,818 and the batch materials used were the same but the amounts differ slightly from those shown in that application. The glass had a coefficient of thermal expansion of about $40 \times 10^{-7}/^{\circ}\text{C}$. The gobs of glass for the canes were obtained from the glass in the tank at the time that the glass had been cooled to about 2275°F. and then remelted in a platinum pot to obtain molten glass from which the cane was pulled. The heat treatment of some of the sample rods to provide a glass-ceramic was in accordance with the process disclosed in U.S. Patent No. 3,380,318. The initial glass had an annealing point of about 1210°F. The rods of glass-ceramic that resulted from the heat treatment were slowly cooled to room temperature over a period of about four hours. This glass-ceramic had an average lineal coefficient of thermal expansion of about $6 \times 10^{-7}/^{\circ}\text{C}$.

Various mixtures of either Duo-Seal pump oil and sodium acetate or paraffin and sodium acetate were heated in a vessel to about 720°F. Of course, at this temperature both were liquid with the pump oil or paraffin as a top layer and sodium acetate as a bottom layer, but with a small amount of sodium acetate in the pump oil or paraffin. The vessel was partially closed by a lid after sample rods of the glass and glass-ceramic were immersed in the oil or paraffin layer. The lid had a small hole in it

for flow escape of decomposition vapors, but the lid provided a positive pressure by these vapors. The sample rods were kept in the vessel for various periods of time with the results tabulated below which show the flexural strength of untreated rods: 5

GLASS RODS

Immersion Unit Hours	—	3	3	3	3	4	5
Sodium acetate wt. %	—	2.5	5	10	20	10	10
Pump oil wt. % or paraffin	—	97.5	95	90	80	90	90
Unabraded strength* (psi) $\times 10^{-3}$	16	40	52	52	57	56	71
Abraded strength* (psi) $\times 10^{-3}$	13	18	27	28	21	50	48
Compressive layer average depth, microns	—	105	98	88	110	124	132

GLASS-CERAMIC RODS

Immersion time, hrs.	—	3	3	3	3	4	5
Sodium acetate, wt. %	—	2.5	5	10	20	10	10
Pump oil wt. % or paraffin	—	97.5	95	90	80	90	90
Unabraded strength* (psi) $\times 10^{-3}$	24	42	52	52	60	70	76
Abraded strength* (psi) $\times 10^{-3}$	20	18	26	32	35	53	57
Compressive layer average depth, microne	—	11	16	22	21	30	22

* to obtain the strengths multiply the indicated numerical values by one thousand, e.g. 16 means a strength of 16000.

- It is seen from the foregoing data that the depth of the compressive stress surface layer may vary widely, e.g., from 10 to 200 microns and yet provide stronger unabraded products. For products subject to abrasion, the best products ordinarily must have other than a thin layer having compressive stress. The minimum value is dependent upon whether the glass has been previously crystallized, as can be seen from the data. For example, a glass-ceramic when alkali metal ion is exchanged to a compressive stress layer depth of 30 microns will retain most of its improved strength upon abrasion, whereas more than 100 microns depth is required for the same glass composition in crystallizable form. In the case of the glass of Example III, 50 microns is an adequate depth. 25
- The following indicates the reason that the present process can be less costly as regards material used. One hundred liters of sodium nitrate weighs 440 pounds and would cost approximately three times the same volume based upon 10 parts by weight of sodium acetate and 90 parts by weight of paraffinic oil. 30

Example II

Glass rods were prepared from a soda-alumina-silica glass composition having the following ingredients in per cent by weight:

5	SiO ₂	57.8
	Al ₂ O ₃	12
	Na ₂ O	22.2
	TiO ₂	8

- This glass was made from batch materials by melting in the conventional manner for this type of glass. The glass had a coefficient of thermal expansion of about $95 \times 10^{-7}/^{\circ}\text{C}$. The glass rods were placed in a vessel in which had been placed 30 grams of potassium acetate per 500 cc. of melted paraffin wax. The following is a tabulation of the test results on the rods after immersion in the melted wax for 2½ hours at about 370°C. (about 700°F)
- Unabraded strength of the glass after the ion exchange was 36,000 psi.
- Unabraded strength of the glass without the ion exchange treatment was 12,000 psi.
- Depth of compression layer was 22 microns.

Example III

- The same procedure as used in Example II was duplicated using glass having the following composition in percent by weight:

30	SiO ₂	48
	Al ₂ O ₃	26
	Na ₂ O	18
	TiO ₂	8

- The glass had a coefficient of thermal expansion of $93 \times 10^{-7}/^{\circ}\text{C}$. The sample rods were treated for 8 hours at 380°C. (about 720°F) and tested and the results are reproduced below:

Strength of glass after ion exchange but before abrading was 69,000 psi.

Strength of the ion-exchanged glass after abrasion was 48,000 psi.

Depth of compression layer was 50 microns.

Due-Seal pump oil is sold by The Welch Scientific Co., Skokie, Illinois for use with vacuum pumps. It is a hydrocarbon oil made for Welch to meet its specifications that are as follows:

Vapor pressure at 50°C. of 0.00001 mm. of mercury

A.P.I. density of 29.3°

Color, N.P.A. of 4.5

Viscosity, S.S.U. at 100°F., of 305—325

Viscosity, S.S.U. at 210°F., of 54

Viscosity Index (Dean & Davis) of 95

Flash point of 410°F.

Fire point of 465°F.

Pour point of 20°F.

Inhibitors—none

- The paraffin wax used in Examples I through III is Sunoco 5512 having a melting point of greater than 150°F. It is sold by Sun Oil Company. It is a narrow boiling range fraction obtained by fractional distillation of paraffin wax obtained in the dewaxing of a motor oil fraction of crude oil.

W. A. Weyl and E. C. Marboe in their book entitled "The Constitution of Glass", volume II, Part One, published in 1964 by Interscience Publishers, a division of John Wiley & Son, inc. New York, N. Y., presents information regarding many types of representative inorganic glasses. A number of these types of inorganic glasses are not the glass used in the present invention, because they do not contain alkali metal oxide and thus are not useful in the present invention which requires an alkali metal oxide, i.e., an alkali metal bonded through oxygen to the basic glass forming structure. Representative of the glasses useful in the present invention are alkali metal silicate glasses, alkali metal silicates containing alkaline earth oxide or oxides in substantial amount, which Weyl and Marboe refer to as alkali-alkaline earth silicates, alkali aluminosilicates, and alkali borosilicates. Other silicate glasses useful in the present invention include alkali metal oxide-zirconia-silica glasses, alkali metal oxide-titania-silica glasses as well as lead-alkali silicate glasses that are referred to on page 4 of the book by E. B. Shand entitled "Glass Engineering Handbook", Second Edition published in 1958 by McGraw-Hill Book Company Inc., New York N. Y. Some of the phosphate glasses contain alkali metal oxide, as can be seen from page 581 of the book by Weyl and Marboe mentioned above and such glasses may be treated by the process of the present invention to form articles of this invention.

It is seen from the foregoing that there are many types of silicate glasses that contain silica and alkali metal oxide. Some contain one or more other oxides that are real or probable glass formers and some contain other oxides as glass modifiers, as those terms are used by Weyl and Marboe. Such chemical elements are shown in Table XXII on page 225 of Volume I (published in 1962) of their book mentioned above. Some contain both other glass formers and other glass modifiers. These silicate glasses containing alkali metal oxide may have compositions that contain the following components in the indicated weight percent ranges.

Percent by Weight

SiO ₂	35—88	115
M ₂ O	1—48	
Al ₂ O ₃	0—40	
CaO	0—15	
MgO	0—28	
BaO	0—15	120
SrO	0—15	
B ₂ O ₃	0—15	
ZrO ₂	0—25	
TiO ₂	0—12	
SnO ₂	0—2	125
P ₂ O ₅	0—10	
As ₂ O ₅	0—3	
Sb ₂ O ₅	0—3	

wherein M_2O refers to the total of alkali metal oxide and, when the alkali metal oxide is lithium oxide, potassium oxide, rubidium oxide or cesium oxide, it constitutes a maximum of 25% by weight of the glass composition. The content of alkali metal oxide to be at least partially replaced in a surface layer by another alkali metal oxide preferably constitutes at least 2% and for glasses, other than glass-ceramics, it is especially preferred that it constitutes at least 5%.

For those glass compositions that are thermally crystallizable to form glass-ceramics, antimony oxide or arsenic oxide is part of the batch material to form the glass. Up to about 1% in total by weight of either or both is used. They are used as fining agent or oxidizing agent. Most of these oxides are lost by vaporization in the glass-making furnace so that the final glass composition will actually contain at most only a few tenths of one percent. When arsenic oxide is used as fining agent there is commonly used also, in the batch, a small amount of sodium nitrate, but it is not normally shown in the list of ingredients.

Fluorine as a salt is commonly used in batch material as an additive in an amount usually not exceeding 0.3% by weight in the final composition. Fluorine is believed to aid crystallization; but its content of the composition is limited to a low value, because it accelerates the crystallization sometimes with an undesirable exothermic effect.

The simplest silicate glass containing alkali metal oxide is the binary type. As pointed out on page 17 of the book entitled "Glass-Ceramics" by P. W. McMillan published in 1964 as a U.S. Edition by Academic Press Inc., New York N. Y., two-component glasses can be prepared for combinations of alkali metal oxides with either silica, boric oxide or phosphorous pentoxide. In the case of silica, there is a limitation on the maximum mole percent of alkali metal oxide as follows: 40% for lithium oxide; 47% for sodium oxide and 50% for potassium oxide. At a higher alkali metal oxide content there will be crystallization or devitrification during cooling of the melt. Replacement of part of one alkali metal by another in such binary glasses, in accordance with the process of the present invention usually would require temperature and time factors economically unfeasible at the present time. Furthermore, mixtures of alkali metal oxides in alkali metal oxide-silica binary glasses have expansion coefficients that show a maximum for a specific ratio and partial exchange of one alkali metal for another could result in no strengthening of the glass. Again it is apparent that the mole percent of silica should not be too high or too low, at least in the case of substitution of potassium for sodium. Such expansion coefficients are shown in Table

LII on page 496 of the book by Weyl and Marboe mentioned above.

In view of the foregoing relating to a binary system, the preferred glasses are used in the present invention are those containing other metal oxides in addition to alkali metal oxide and silica. The following presents various examples of multicomponent glass systems.

One example is the class of glasses composed of silica, one or more alkali metal oxide, and one or more alkaline earth metal oxide. A common glass representative of this class is the alkali-lime-silica glass, such as used for window sheet glass, plate glass and container glass. In these commercial glasses the alkaline earth metal oxide content is usually lime or a mixture of calcia and magnesia such as is present in a dolomitic lime. The approximate composition of such commercial glasses on a weight basis is as follows:

70—74% silica, 12—16% soda, either 10—13% calcia and magnesia total or 8—12% calcia and 1—4% magnesia. Alumina is present in an amount of 0.5—1.5% by weight for sheet and plate glass while for container glass it is usually 1.5—2.5%, but in some cases exceeds 5%. This glass with the low alumina content can be ion exchanged to improve its strength but upon abrasion most, if not all, of the increased strength is lost and thus the ion exchange treatment is suitable only when the product is not subjected to abrasion during its use. However, it is possible to provide an alkali metal oxide-alkaline earth metal oxide-silica glass, containing such small amount of alumina or containing no alumina, that by ion exchange has an improved strength, even after a substantial degree of abrasion.

Another class of glasses within the broad type of alkali metal silicate glasses is the lead-alkali metal silicate glass, in which the alkali metal oxide is potassium oxide alone or with soda, i.e. sodium oxide, as shown in Table I—1 on page 4 of Shand's book mentioned above. Similarly, another class of glasses is the borosilicate glass system which is illustrated by glasses numbers 10, 11 and 12 in Table I—1 of the above-mentioned book.

Another class of glasses useful in the present invention is the alkali aluminosilicate glass compositions which are disclosed in French Patent No. 1,329,124 and South African Patent No. 62/2353. The above patents disclose as the broad range for such compositions on a weight basis: 50—75% silica; at least 5% and preferably from 10—25% alumina; and at least 5% preferably 10—25% Na_2O , with the alumina and Na_2O content preferably constituting at least 15% of the glass composition and with these two plus the silica constituting at least 85% of the glass composition. It is indicated that divalent metal oxides, potassium oxide, boron oxide, titania, phosphorous pentoxide and fluorine may be

present up to a maximum individual content of 10% and collectively up to a maximum of 15%. It is also stated that lithium oxide may be present but should not exceed 1%. Because some of these limitations are based upon the attaining of the high strength even after abrasion, such limitation, although preferred, is not a limitation on the present invention.

Another class of glasses of the broad alkali metal oxide-silica type is the lithium silicate glass described in French Patent No. 1,329,125 and South African Patent No. 62/2352. These particular patents disclose that this glass contains on a weight basis 46—88% silica and 4—29% lithia. This glass may contain alumina to constitute the remainder, if any, but the ratio of silica to alumina should be at least 2:1. Thus it is seen that this class of glasses can be the binary type mentioned above, but when alumina is present it is the alkali metal aluminosilicate also mentioned above. Instead of alumina, or for part of it, there may be present one or more of the following constituents: zirconia; titania; and boron oxide. In addition other alkali metal oxides, namely, sodium oxide and potassium oxide, may be present along with lead oxide (PbO) and fluorine up to a total of 15 mole percent. Of course, some of these limitations relate to the compositions which provide the maximum mechanical strength after abrasion, but such is not a limitation for the present invention in its broadest sense.

A further class of glasses that contain ion exchangeable alkali metal ions is the glass composition disclosed in French Patent No. 1,329,126 and South African Patent No. 62/2354. This glass composition is described as constituting at least 10%, preferably at least 20%, by weight of zirconia and the balance silica, except for lithia (lithium oxide), if present, which normally should not exceed 1% by weight and except for optional compatible ingredients including divalent metal or oxides, potassium oxide, boron oxide, phosphorus pentoxide, titania and fluorine which individually may be present in an amount up to 10 percent by weight and collectively may be present in an amount up to 15% by weight. In the ternary glass system the composition can be, e.g. 60 to 75% by weight of silica, 5 to 20% by weight of zirconia and 20% by weight of sodium oxide.

French Patent No. 1,375,995 discloses that alkali-alkaline earth metal silicate glasses, which may contain alumina, boron oxide and various compatible inorganic oxides, can be ion exchanged using alkali metal salts. These glasses contain by weight in excess of 40%, e.g. 65—75% silica, 0—15% boron oxide, 0—35% alumina, 0—25% calcium oxide, magnesium, strontia, barium oxide, lead oxide and/or zinc oxide and combinations thereof, 0—10% titania, 0—10% potassium oxide and 2—20% sodium oxide and/or lithium oxide.

Typical glass compositions are described and these are ion exchanged for strengthening of the glass.

South African Patent No. 63/5619 discloses glass compositions, which are capable of ion exchange. These compositions contain by weight 65—75% silica, 10—20% sodium oxide, 0—5% potassium oxide, 3—15% calcium oxide, 0—10% magnesia, 0—5% alumina and 0—5% barium oxide. Some of the sodium oxide can be replaced by additional potassium oxide.

South African Patent No. 63/5747 discloses another class of glass compositions which are alkali silicates that contain magnesia and/or zinc oxide, with or without alumina. In these compositions alkaline earth metal oxides may be absent. These glasses are stated as containing by weight in excess of 40%, e.g., 55—75% silica, 0—40% alumina, 0—25% calcium oxide, magnesia, strontia, barium oxide, lead oxide and/or zinc oxide and combinations thereof, 0—10% titania, 0—10% potassium oxide, and 2—20% sodium oxide and/or lithium oxide. A representative range for such glass composition is as follows:

Percent by Weight		
SiO ₂	55—70	
Al ₂ O ₃	1—30	
MgO and/or ZnO	3—10	95
Li ₂ O	2—8	
Na ₂ O	4—8	
K ₂ O	0—2	

South African Patent No. 63/5619 relates to similar glass compositions that required to be lithia-containing. A representative range for such glass compositions is as follows:

Percent by Weight		
SiO ₂	55—75	
Li ₂ O	3—20	105
Na ₂ O	1—22, when present	
K ₂ O	0—5	
Al ₂ O ₃	10—30, when present	
MgO and/or ZnO	0—5	
ZrO ₂	3—20, when present	110
Al ₂ O ₃ and ZrO ₂	13—33	

with mole ratio of Li₂O:Na₂O between 0.2:1 to 5:1 and fluorine as fining agent is present when alumina is present. In addition to the above oxides, such glasses can contain by weight: 0—10% titania; 0—3% barium oxide and/or lead oxide; and 0—1% Sb₂O₃, As₂O₃, phosphorus pentoxide and fluorine. Calcium oxide in an unstated amount may be present. Usually when both lithia and soda are present, their combined total ranges from 5—25% by weight.

The glass-ceramics preferably used in the present invention are opaque or translucent. Especially preferred are the opaque glass-ceramics which contain a multiplicity of

- crystals in a glassy matrix wherein the average diameter of the individual opaque crystals is less than 30 microns across the largest dimension. The average lineal coefficient of thermal expansion of these opaque glass-ceramics is generally less than $20 \times 10^{-7}/^{\circ}\text{C}$. (between 25°C and 300°C).
- Examples of thermally crystallizable silicate glass compositions are given in U.S. Patent No. 2,920,971. On the basis of the actual contents of various ingredients of these glasses presented in that Patent the range of the compositions is as follows:
- | | | Percent by Weight | |
|----|-------------------------|-------------------|--|
| 15 | SiO_2 | 56.1—73.1 | |
| | Al_2O_3 | 12.1—15.3 | |
| | Li_2O | 3.0—5.2 | |
| | Na_2O | 0—1.7 | |
| | K_2O | 0—0.2 | |
| 20 | CaO | 0—11.1 | |
| | MgO | 0—8.8 | |
| | TiO_2 | 4.5—13.8 | |
| | ZrO_2 | 0—3.9 | |
- In some of these compositions fluorine is present as a fining agent. These compositions after controlled thermal crystallization are glass-ceramics and some of these, provided there is suitable heat treatment, are capable of ion exchanging lithium in the glass-ceramic with an alkali metal in an inorganic salt bath and thus capable of being ion exchanged by the method of the present invention.
- U.S. Patent No. 3,157,522 discloses a class of glass and glass-ceramic therefrom. The range for the composition is as follows:
- | | | Percent by Weight | |
|----|-------------------------|-------------------|--|
| | SiO_2 | 55—75 | |
| | Al_2O_3 | 12—36 | |
| 40 | Li_2O | 2—15 | |
| | TiO_2 | 3—7 | |
- with the recited ingredients constituting at least 95% of the composition and the weight ratio of $\text{Li}_2\text{O}:\text{Al}_2\text{O}_3$ being between 0.1:1 and 0.6:1.
- Another class of thermally crystallizable glass compositions that can be ion exchanged in the glass form and by proper heat treatment can be exchanged as a glass-ceramic is set forth below. The range of this composition is as follows:
- | | | Percent by Weight | |
|--|-------------------------|-------------------|----|
| | SiO_2 | 48—73 | |
| | Al_2O_3 | 14—35 | |
| | Li_2O | 4—10 | |
| | ZrO_2 | 2—6 | 55 |
- and wherein the sum of recited ingredients, other than zirconia, is greater than 85% of the composition.
- Belgian Patent No. 609,529 describes another thermally crystallizable glass composition having the following composition:
- | | | Percent by Weight | |
|--|-------------------------|-------------------|----|
| | SiO_2 | 48—73 | |
| | Al_2O_3 | 14—25 | |
| | Li_2O | 4—10 | |
| | TiO_2 | 0—1.8 | |
| | ZrO_2 | 2—6 | 65 |
- wherein the total of the recited ingredients, other than titania and zirconia, constitutes at least 85% of the glass. Many of the specific compositions that are disclosed contain 3% by weight of B_2O_3 .
- Belgian Patent No. 633,889 discloses thermally crystallizable glass compositions and glass-ceramics therefrom, both of which can be ion exchanged to replace one alkali metal ion by another. Such compositions contain silica, alumina, lithium oxide, boron oxide and 3—7% by weight of MgO and/or ZnO plus a small quantity of a nucleating agent. The typical composition range indicates that the silica content would be 55—66% by weight, the alumina content would be 13—22% by weight and the lithium oxide content would be 2.5—5% by weight.
- Another class of thermally crystallizable glass compositions that is ion exchangeable is disclosed in U.S. Patent No. 3,170,805 in which the major constituents are silica, lithium oxide and zinc oxide in the weight percent ranges of 34—81, 2—27 and 10—59, respectively. Other constituents may be present as indicated, and P_2O_5 in the amount of 0.5—6% by weight where metallic nucleating agents are used.
- The amount of nucleating agent, such as titania and zirconia, depends upon the particular composition and the particular nucleating agent or combination of nucleating agents, etc. Metal oxides as colorants may be present in an amount of 0.005—2% by weight. To provide lower expansion characteristics to the glass-ceramic that can be formed from the glass composition, the components are as follows:

Percent by Weight	
SiO ₂	56—68
Al ₂ O ₃	18—27
Li ₂ O	3.4—4.5
CaO	0—3
ZnO	0—2
B ₂ O ₃	0—4
TiO ₂	0—6
ZrO ₂	0—3
MgO	0—3
Na ₂ O	0—1
P ₂ O ₅	0—3
(SiO ₂ and Al ₂ O ₃)	at least 82
(SiO ₂ , Al ₂ O ₃ , B ₂ O ₃ and P ₂ O ₅)	86—91
(CaO, MgO, ZnO, and Na ₂ O)	2.5—6
(SiO ₂ , Al ₂ O ₃ , P ₂ O ₅ and Li ₂ O)	no more than 93
TiO ₂ and ZrO ₂	2—6

where the ratio of (CaO, MgO, ZnO, Na₂O and B₂O₃) to Li₂O is less than 2.4 and the ratio of SiO₂ to Al₂O₃ is no more than 3.3 and preferably no more than 3.8.

- 5 Another class of glass compositions as thermally crystallizable glass and as glass-ceramics is the subject of U.S. Patent No. 3,380,818. The composition consists essentially of the following:

Percent by Weight	
SiO ₂	66—73
Al ₂ O ₃	15—19
Li ₂ O	2.5—4
15 MgO	3—7.7
ZrO ₂	1—1.7
TiO ₂	1—<1.9
SnO ₂	0—1.7
P ₂ O ₅	0—3
20 BaO	0—5
ZnO	0—3

where the total weight percent of ZrO₂, TiO₂, SnO₂ and P₂O₅ is at least 2.8, and the total weight percent Li₂O and MgO is 6.3 to 10.5.

- 25 The glass compositions in the paragraphs immediately preceding form glass-ceramics

containing beta-eucryptite and/or beta-spodume. Glass compositions have been developed for thermally crystallizable glass-ceramics in which the crystals or crystallites or other materials including those are nepheline. Such glass compositions at least as a thermally crystallizable glass can be ion exchanged. One class of such compositions is as follows. This composition contains the following ingredients:

30

35

Percent by Weight	
SiO ₂	44—52
Al ₂ O ₃	22—29
Na ₂ O	15—22
TiO ₂	6—12
K ₂ O	0—3
SiO ₂ and Al ₂ O ₃	69—76
Na ₂ O and K ₂ O	17—22

40

where the weight ratio of SiO₂ to (Na₂O and K₂O) is between 2.1 and 3, and the mole ratio of (Na₂O and K₂O) to Al₂O₃ is at least 1.02. The usually preferred Na₂O range is 16—21% by weight

45

Another class of glass compositions that form nepheline as a crystal phase in a glass-ceramic contains the following ingredients:

50

	Percent by Weight	
	SiO ₂	45—57
	Al ₂ O ₃	29—38
	Na ₂ O	13—22
5	TiO ₂	1—3*
	ZrO ₂	1—4*
	BaO	2—14*
	SiO ₂ , Al ₂ O ₃ and Na ₂ O	at least 95
10	* in excess over 100% of the sum SiO ₂ , Al ₂ O ₃ and Na ₂ O. Li ₂ O, K ₂ O, P ₂ O ₅ and bivalent metal oxides may be present in total less than 5%.	
15	British Patent No. 869,328 discloses glass compositions that can be ion exchanged by replacing an alkali metal ion. Such a glass system contains sodium oxide, alumina and silica with titania as a nucleating agent in combination with one or more other agents. The Na ₂ O content is 7—34 mole percent. Metal	
20	oxides used in combinations with titania are listed in the British Patent and it is indicated that they must constitute at least 1.9 mole percent in excess of the total moles of silica, alumina, sodium oxide, potassium oxide and	
25	calcium oxide in the glass composition to provide a controlled thermally, crystallizable glass. When crystallized the glass-ceramic contains a nepheline crystal phase.	
30	The term "strain point" is defined on page 659 of the book by Weyl and Marboe mentioned above and in U.S. Patent No. 2,779,136.	
	WHAT I CLAIM IS:—	
35	1. A process for treating an article composed of an inorganic glass (as hereinbefore defined) containing an alkali metal oxide, which process comprises contacting a surface of said glass with a non-polar, non-ionic liquid medium containing a different alkali metal as	
40	a salt of an organic acid at an elevated temperature and for a period of time sufficient for some of said alkali metal in the surface layer only to exchange with some of said different alkali metal in said salt, removing the salt, and	
45	cooling the glass article.	
	2. The process of claim 1 wherein the inorganic glass is a silicate glass and the alkali metal oxide in said glass constitutes at least 1% by weight of the glass at least in said	
50	surface layer.	
	3. The process of claim 2 wherein said liquid medium comprises said salt as a minor constituent and an organic vehicle as a major constituent.	
55	4. The process of claim 3 wherein said organic vehicle is at least one non-polar, non-ionic organic compound.	
	5. The process of claim 4 wherein said vehicle is a paraffin in hydrocarbon oil.	
60	6. The process of claim 4 wherein said vehicle is a paraffin wax.	
	7. The process of any of claims 1 to 6 wherein said organic acid is a carboxylic acid.	
	8. The process of claim 7 wherein said carboxylic acid is acetic acid.	
	9. The process of claim 8 wherein said salt is sodium acetate and said alkali metal in said glass is lithium and said elevated temperature is below the strain point of said glass.	
	10. The process of claim 9 wherein said elevated temperature is between 200°C. and 550°C.	
	11. The process of claim 12 wherein said elevated temperature is between 300°C and 430°C. and the period of time is at least three hours.	
	12. The process of any of claims 9 to 11 wherein said glass is a glass-ceramic.	
	13. The process of claim 12 wherein said glass ceramic is opaque and contains a multiplicity of crystals, each crystal being less than 30 microns across its largest dimension, and said glass-ceramic has an average lineal coefficient of thermal expansion that is less than 20×10^{-7} per °C. (between 25°C. and 300°C.).	
	14. The process of any of claims 9 to 11 wherein said glass is a thermally crystallizable glass.	
	15. The process of claim 8 wherein said glass is a soda-alumina-silica glass containing titania, wherein said salt is potassium acetate, and wherein said elevated temperature is below the strain point of the glass.	
	16. The process of claim 15 wherein said elevated temperature is between 371°C. and 400°C. and the period of time is at least 3 hours.	
	17. A process for treating an article composed of a glass containing as its ingredients the following in weight percent ranges:	
	SiO ₂	35—88
	M ₂ O	1—48
	Al ₂ O ₃	0—40
	CaO	0—15
	MgO	0—28
	BaO	0—15
	SrO	0—15
	B ₂ O ₃	0—15
	ZrO ₂	0—25
	TiO ₂	0—12
	SnO ₂	0—2
	P ₂ O ₅	0—10
	As ₂ O ₅	0—3
	Sb ₂ O ₃	0—3,
	the balance, if any, being other compatible ingredients and	
	wherein M ₂ O refers to the total of alkali metal oxide, which comprises immersing for a period of time the glass article in a liquid body of a non-polar, non-ionizing organic vehicle containing as a minor percentage an alkali metal salt of an organic acid while maintaining said body at an elevated temperature, said alkali metal of said salt being a different chemical element than an alkali metal present in said	

- glass in an amount of at least 1% by weight expressed as oxide, and said temperature and time being sufficient for ion-exchange by said different chemical elements to occur between a surface layer only of said glass and said salt in said liquid body of an organic vehicle, removing the glass article, and removing any adhering organic vehicle and salt.
18. The process of claim 17 wherein said organic vehicle is a hydrocarbon material, the organic acid of the salt is a carboxylic acid, the temperature is between 300°C. and 430°C. and the period of time of immersion is at least three hours.
19. The process of claims 17 or 18 wherein said minor percentage is less than 1% by weight, said different chemical elements in the glass and salt are lithium and sodium, respectively, and the acid is acetic acid.
20. The process of any of claims 17 to 19 wherein said glass is a thermally crystallizable glass.
21. The process of any of claims 17 to 19 wherein the glass in an opaque glass-ceramic containing a multiplicity of crystals, each being less than 30 microns across its largest dimension, and having an average lineal coefficient of thermal expansion that is less than 20×10^{-7} per °C. (between 25°C. and 300°C.).
22. The process of any of claims 17 or 18 wherein said salt is potassium acetate, said glass is a soda-alumina-silica composition containing titania.
23. A glass article having a compressive stress surface layer obtained by the process of any of claims 1 to 22.
24. A process as defined in any of claims 17 to 21 in which the organic vehicle is paraffin wax.
25. A process for treating an article composed of an inorganic glass containing an alkali metal oxide substantially as hereinbefore described with reference to and as illustrated in the foregoing examples.
26. A glass article whenever treated by a process as claimed in any one of claims 1 to 22, 24, or 25.

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